

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re: Patent Application of : PATENT APPLICATION  
CHARLES B. GREENBERG, et al. :  
Serial No.: *to be assigned* : Group Art Unit: 1775  
Filed: *filed herewith* : Examiner: J. McNeil  
For: PHOTOCATALYTICALLY-ACTIVATED :Attorney Docket 1240D2  
SELF-CLEANING ARTICLE AND :  
METHOD OF MAKING SAME :  
:

PRELIMINARY AMENDMENT

Commissioner for Patents  
Washington, DC 20231

Sir:

Please amend the captioned application in the below-  
indicated manner.

IN THE SPECIFICATION

Please replace the paragraph beginning at line 5, page 1, with  
the following paragraph.

This application is a divisional of U.S. Application  
Serial No. 09/282,943 filed April 1, 1999, which is a  
divisional of U.S. Non-provisional Application Serial No.  
08/899,257 filed July 23, 1997, now U.S. Patent No, 6,027,766,  
which claims the benefit of U.S. Provisional Application  
Serial No. 60/040,566 filed March 14, 1997. U.S. Provisional  
Application Serial No. 60/040,565 filed March 14, 1997, and  
U.S. Regular Application No. 08/899,265 to Greenberg et al.,  
entitled "Photocatalytically-Activated Self-Cleaning  
Appliances", filed even date herewith, now U.S. Patent No.  
6,054,227 are also related to the present application and are  
hereby incorporated by reference.

Please amend the specification in the following 9 ways.

1) Please replace the paragraph beginning at page 5, line 33, with the following rewritten paragraph:

The PASC coating 24 must be sufficiently thick so as to provide an acceptable level of PASC activity. There is no absolute value which renders the PASC coating 24 "acceptable" or "unacceptable" because whether a PASC coating has an acceptable level of PASC activity is largely determined by the purpose and conditions under which the PASC coated article is being used and the performance standards selected in connection with that purpose. In general, thicker PASC coatings provide higher PASC activity. However, other considerations may weigh toward a thinner coating, e.g. thinner coatings are preferred when the article is to have high transmission for aesthetic or optical reasons; the surface contaminants on the surface of the article are easily removed with a thinner PASC coating, the coating is exposed to substantial irradiation and/or the PASC coating 24 will be exposed to sodium ion poisoning discussed in more detail below. In a CVD process, a photocatalytically-active self-cleaning coating 24 is formed which may range from about 100Å to 2500Å thick. For a wide variety of applications, it is preferred that the PASC coating is at least about 200 Angstroms (Å), preferably at least about 400Å and more preferably at least about 500Å thick. It has been found that when the substrate 22 is a piece of float glass and the PASC coating 24 is an anatase titanium dioxide PASC coating formed directly over the piece of float glass by the CVD method, that a thickness of at least about 500Å provides a PASC reaction rate in the range of about  $2 \times 10^{-3}$  to about  $5 \times 10^{-3}$  per centimeter minute (hereinafter " $\text{cm}^{-1}\text{min}^{-1}$ ") for the removal of a stearic acid test film when the PASC coating was exposed to ultraviolet radiation from a light source such as that sold under the tradename UVA-340 by the Q-Panel Company of Cleveland, Ohio, having an intensity of about 20 watts per square meter (hereinafter  $\text{W/m}^2$ ) at the PASC coating surface which is acceptable for a wide range of applications.

2) Also please replace the paragraph beginning at page 47, line 6, with the following paragraph:

The results of the photocatalytic analysis shown in Table 6 suggest that a titanium dioxide layer thickness of about 625Å with no barrier layer (Sample I) can approach the PASC activity of a thinner 400Å PASC coating over an SIDB layer (Sample J). It should be noted that for Samples J, the SIDB layer underwent an intermediate cooling and subsequent reheating operation described, which reheating operation may have reduced the SIDB layer effectiveness for Sample J, which might otherwise have had a higher PASC activity.

3) Please replace the paragraph beginning at page 15, line 5, with the following paragraph:

Referring now to Fig. 2, in an alternative method of preventing sodium ion poisoning of the PASC coating, an SIDB layer 26 is provided between the PASC coating 24 and the substrate 22. The SIDB layer 26 may be the only layer between the PASC coating 24 and the substrate 22, or it may be one layer of a multilayer stack. Where a multilayer stack is employed, it is not required that the SIDB layer 26 be in contact with the substrate 22, provided the SIDB layer 26 is positioned between the PASC coating 24 and the substrate 22 to prevent sodium ion numeral 27 as depicted in Fig. 2 migration from the substrate 22 to the PASC coating 24.

4) Please replace the paragraph beginning at page 28, line 1, with the following paragraph:

The decreased PASC activity of Example 2 is believed to arise from the difference in titanium dioxide coating thickness between Examples 1 and 2, (about 2100Å versus about 700-800Å, respectively). More particularly, it is believed that the PASC reaction rate of Example 2 was lower than that

of Example 1 due to the increased depth of sodium ion diffusion into the titanium dioxide coating of Example 2 as a larger percentage of the total thickness of the titanium dioxide PASC coating for the titanium dioxide PASC coating of Example 2 than that of Example 1. It is believed that sodium ions migrated from the glass sample into the PASC coating of Example 2 in annealing zone 98. One conclusion that may be drawn from a comparison of Examples 1 and 2 is that in the absence of an SIDB layer, thicker PASC coatings are less susceptible to sodium ion poisoning, thus maintaining higher PASC activity.

5) Also, if not already present in the captioned patent application, please replace the paragraph beginning at page 12 line 29 with the following rewritten paragraph which includes added sentences and also adds the following additional paragraphs:

The preferred method to provide a PASC coating using the MSVD method is to sputter a coating on the substrate, remove the coated substrate from the MSVD coater and thereafter heat treat the coated substrate to crystallize the sputter coating into the PASC coating 24. For example, but not limiting to the invention, with the MSVD method, a target of titanium metal sputtered in an argon/oxygen atmosphere having about 5-50%, preferably about 20% oxygen, at a pressure of about 5-10 millitorr to sputter deposit a titanium dioxide coating of desired thickness on the substrate 22. The coating as deposited is not crystallized. The coated substrate is removed from the coater and heated to a temperature in the range of about 400°C (752°F) to about 600°C (1112°F) for a time period sufficient to promote formation of the PASC crystalline form of titanium dioxide to render PASC activity. Generally at least an hour at temperature in the range of about 400°C (752°F) to about 600°C (1112°F) is preferred. Where the substrate 22 is a glass sheet cut from a glass float ribbon,

the PASC coating 24 may be sputter deposited on the air side and/or the tin side.

The substrate 22 having the PASC coating 24 deposited by the CVD, spray pyrolysis or MSVD methods may be subsequently subjected to one or more post-PASC coating annealing operations to increase the self-cleaning activity of the PASC coating 24. It is believed that such post-PASC coating annealing may increase self-cleaning activity of the PASC coating 24 by promoting formation of the desired PASC crystalline phase. As may be appreciated, the time and temperatures of the anneal may be affected by several factors, including the makeup of substrate 22, the makeup of PASC coating 24, the thickness of the PASC coating 24, and whether the PASC coating 24 is directly on the substrate 22 or is one layer of a multilayer stack on substrate 22. It has been determined that where the substrate 22 is a piece of float glass and the PASC coating is a 400Å or 625Å thick anatase titanium dioxide formed by the spray pyrolysis method, that annealing the coating at 500°C (932°F) for up to 13 minutes increased PASC activity.

As discussed above, whether the PASC coating is provided by the CVD process, the spray pyrolysis process or the MSVD process, where the substrate 22 includes sodium ions that can migrate from substrate 22 into the PASC coating deposited on substrate 22, the sodium ions may inhibit or destroy the photocatalytic activity of the PASC coating by -

6) Also if not already present in the captioned patent application, please replace the section of the paragraph beginning at page 14 line 1 with the following full paragraph:

--As discussed above, whether the PASC coating is provided by the CVD process, the spray pyrolysis process or the MSVD process, where the substrate 22 includes sodium ions that can migrate from substrate 22 into the PASC coating deposited on substrate 22, the sodium ions may inhibit or destroy the photocatalytic activity of the PASC coating by

forming inactive compounds while consuming titanium e.g. by forming sodium titanates or by causing recombination of photoexcited charges.--

7) Also if not already present in the captioned patent application, please replace the paragraph beginning on page 14 line 10 with the following rewritten paragraph which includes additional sentences and which is followed by additional paragraphs:

--It has been found that when the thickness of the PASC coating exceeds a minimum threshold value, the PASC activity is not destroyed by sodium ion migration even though the PASC coating is deposited over the surface of a sodium-ion containing substrate while the substrate is at a temperature sufficient to cause migration of sodium ions from substrate into the PASC coating. While the mechanism for this result is not completely understood, it is believed that when the thickness of the PASC coating exceeds this minimum thickness, the sodium ions are able to migrate only through a fraction of the overall thickness of the PASC coating during the time period at which the temperature of substrate exceeds the temperature which permits sodium ion migration. Thereafter, when the temperature of substrate falls below that which causes sodium ion migration, the sodium ions migration stops or "freezes" in place, resulting in a thickness of the PASC coating opposite from the substrate surface free of sodium ion poisoning and able to maintain PASC activity. This minimum thickness of the PASC coating as may be appreciated by those skilled in the art varies with expected parameters such as, but not limited to, the time at which substrate is held above the temperature at which sodium ion migration occurs, the use to which the PASC article of manufacture is to be put and the degree of PASC activity desired or required. It has been found that for a CVD deposited titanium dioxide PASC coating over a piece of soda-lime-silica flat glass, the thickness of the PASC coating should be a minimum of about 250Å, preferably

a minimum of about 400Å and more preferably a minimum of about 500Å to permit a sufficient portion of the PASC coating 24 to remain free of sodium ion poisoning and retain its PASC activity.

Referring now to Fig. 2, in an alternative method of preventing sodium ion poisoning of the PASC coating, an SIDB layer 26 is provided between the PASC coating 24 and the substrate 22. The SIDB layer 26 may be the only layer between the PASC coating 24 and the substrate 22, or it may be one layer of a multilayer stack. Where a multilayer stack is employed, it is not required that the SIDB layer 26 be in contact with the substrate 22, provided the SIDB layer 26 is positioned between the PASC coating 24 and the substrate 22 to prevent sodium ion migration from the substrate 22 to the PASC coating 24.-

8) Also if not already present in the captioned patent application, please replace the section of the paragraph that begins on page 16 line 1 and ends on page 16 line 9 with the following complete paragraph:

--The SIDB layer 26 may be formed of amorphous or crystalline metal oxides including but not limited to cobalt oxides, chromium oxides and iron oxides, tin oxides, silicon oxides, titanium oxides, zirconium oxides, fluorine-doped tin oxides, aluminum oxides, magnesium oxides, zinc oxides, and mixtures thereof. Mixtures include but are not limited to magnesium/aluminum oxides and zinc/tin oxides. As can be appreciated by those skilled in the art, the metal oxide may include oxides, super-oxides or sub-oxides of the metal. While the thickness of the SIDB layer necessary to prevent sodium ion poisoning of the PASC coating varies with several factors including the time period at which a substrate will be maintained at temperatures above which sodium ion migration occurs, the rate of sodium ion migration from the substrate, the rate of sodium ion migration through the SIDB layer, the thickness of the PASC coating and the degree of photocatalytic

activity required for a given application, typically for most applications, the SIDB layer thickness should be in the range of at least about 100Å, preferably at least about 250Å and more preferably at least about 500Å thick to prevent sodium ion poisoning of the PASC coating layer. The SIDB layer may be deposited over substrate 22 by CVD, spray pyrolysis, or MSVD methods. Where the spray pyrolysis or CVD methods are employed, the substrate 22 is preferably maintained at a temperature of at least about 400°C (752°F) to ensure decomposition of the metal-containing precursor to form the SIDB layer. The SIDB layer may be formed by other methods, including the sol-gel method, which sol-gel method as noted above is not compatible with the manufacture of a glass float ribbon.-

9) At page 12 after line 28 of the captioned patent application after the word "method", please insert the following paragraphs from U.S. Patent 4,379,040 column 7 line 42 through column 8 line 44 which was incorporated by reference in the specification at page 12 line 5:

--It was customary to attain a desired degree of oxidation in titanium oxide films by an evaporation technique carried out in two distinct stages; first, by depositing titanium oxide in an under-oxidized state and thereafter, by introducing an oxidizing atmosphere thereto to attain the desired degree of oxidation. It has been found according to the present invention that the titanium oxide can be successfully magnetically enhanced sputtered onto the substrate with the degree of oxidation desired, thus eliminating the need for further oxidation. Deposition of ideally oxidized titanium oxide films is also more easily controlled in the practice of the present invention than heretofore, yielding a more consistent final product. It is believed that the preferred titanium oxide films deposited according to the present invention comprise a combination of titanium dioxide intermixed with atoms and/or small



agglomerations of titanium metal, i.e. films of titanium oxide having greater than 1.7 but less than 2.0 parts oxygen to parts titanium, and preferably between 1.9 and 2.0. Such films may be characterized as having an optical extinction coefficient between about 0.03 and 0.3, preferably between 0.03 and 0.09, and most preferably between 0.06 and 0.08. The titanium oxide layer is preferably deposited with a thickness within the range of about 200 to 500 Angstroms to obtain the desired optical properties and film continuity.

The titanium oxide layer can be deposited according to the present invention by magnetically sputtering a titanium metal cathode in an evacuated atmosphere having partial pressures of oxygen and argon. Initially, the coating chamber 12 is evacuated to less than  $3 \times 10^{-5}$  torr, after which an atmosphere of about 75% argon and 25% oxygen at a total pressure of about  $6 \times 10^{-4}$  torr is established. The cathode is activated at a preselected constant electrical power, and the deposition rate and total chamber pressure are established at preselected values. Upon reaching the desired coating conditions, the cathode is scanned across the surface of the substrate at a preselected rate to deposit a thin layer of an ideally oxidized film thereon. The luminous transmittance of the substrate is monitored during deposition by the photometer and photoelectric cell and decreases as the thickness of the film increases, from an initial value of about 90% for a glass substrate. Deposition rate, and therefore the degree of oxidation of the deposited titanium oxide film, is maintained constant either cyclically, or continuously, utilizing the embodiment of the invention. Deposition of the titanium oxide layer can be terminated when the luminous transmittance decreases to a value between about 72% and 76%, (about 80% to 85% of the transmittance of the uncoated substrate) a condition which is usually reached with a film thickness between about 300 Å and 350 Å, entailing about 5 to 7 passes of the cathode over the substrate. Generally during the above-described procedure, the oxygen input rate is gradually increased to compensate for decreasing amounts of outgassing

from the coating chamber. The titanium oxide layer can have has an optical extinction coefficient between about 0.06 and 0.08 upon deposit, according to the present invention. --

#### IN THE CLAIMS

Cancel claim 1 without prejudice and insert following new claims 57-89, 112-119, 121 and 122.

57. A method comprising the steps of:

manufacturing a continuous glass float ribbon having a first major surface and an opposite major surface defined as a second major surface, the first major surface having tin diffused therein characteristic of forming the glass float ribbon on a molten tin bath,

positioning a chemical vapor deposition coating apparatus over the surface of the float ribbon at a point in the manufacture of the float ribbon where the float ribbon has a temperature of at least about 400° C (752° F);

directing a metal oxide precursor selected from the group consisting of titanium tetrachloride, titanium tetraisopropoxide and titanium tetraethoxide in a carrier gas stream through said chemical vapor deposition apparatus over a surface of the float ribbon and annealing the float ribbon to produce titanium dioxide in the crystalline phase as a photocatalytically-activatable self-cleaning coating over the glass float ribbon,

whereby said coating is capable of having a photocatalytically-activated self-cleaning reaction rate of least about  $2 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$ .

58. A method comprising the steps of:

manufacturing a continuous glass float ribbon having a first major surface and an opposite major surface defined as a second major surface, the first major surface having tin diffused therein characteristic of forming the glass float ribbon on a molten tin bath;

depositing a photocatalytically-activatable self-cleaning coating over at least one of the major surfaces by positioning a spray pyrolysis coating apparatus over the surface of the float ribbon at a point in the manufacture of the float ribbon where the float ribbon has a temperature of at least about 400° C (752° F), directing an aqueous suspension of titanyl acetylacetonate and wetting agent in an aqueous medium, wherein the concentration of the titanyl acetylacetonate is in the range from about 5 to about 40 weight percent of the aqueous suspension, through said spray pyrolysis coating apparatus over a surface of the float ribbon and annealing the float ribbon in air to produce titanium dioxide in the crystalline phase as a photocatalytically-activatable self-cleaning coating over the glass float ribbon, whereby said coating is capable of having a photocatalytically-activated self-cleaning reaction rate of at least about  $2 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$ .

59. In a method for forming a glass float ribbon wherein the method includes the steps of melting glass batch materials in a furnace; delivering the molten glass onto a bath of molten tin; pulling the molten glass across the tin bath whereupon the glass is sized and controllably cooled to form a dimensionally stable glass float ribbon; removing the float ribbon from the tin bath; moving the float ribbon by conveying roller through a lehr to anneal the float ribbon; moving the float ribbon to a cutting station on conveying rollers where the ribbon is cut into glass sheets, the improvement comprising:

depositing by a process selected from the group consisting of spray pyrolysis and chemical vapor deposition a crystalline phase of a photocatalytically-activatable self-cleaning coating over a surface of said float ribbon as the float ribbon is formed, whereby said coating is capable of having a photocatalytically-activated self-cleaning reaction rate of at least about  $2 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$ .

60. A method comprising the steps of:

providing a glass article having at least one surface by a float manufacturing process;

depositing a photocatalytically-activatable self-cleaning coating over the surface of the article by a process selected from the group consisting of chemical vapor deposition and spray pyrolysis during the glass manufacturing process so that the coating has titanium dioxide in the crystalline phase and has a thickness in the range of at least 200 Å and less than 1 micron whereby said coating is capable of having a photocatalytically-activated self-cleaning reaction rate of at least about  $2 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$ .

61. A method comprising the steps of:

providing an article of manufacture having at least one surface;

depositing a sodium ion diffusion barrier layer by a process selected from the group consisting of chemical vapor deposition, magnetron sputtered vacuum deposition (MSVD), and spray pyrolysis having a thickness of at least 100 Å over said surface; and

depositing a photocatalytically-activatable self-cleaning coating by a process selected from the group consisting of chemical vapor deposition, MSVD, and spray pyrolysis over said sodium ion diffusion barrier layer whereupon said sodium ion diffusion barrier layer inhibits migration of sodium ions from the surface of said article to said photocatalytically-activatable self cleaning coating.

62. In a method for forming a glass float ribbon wherein the method includes the steps of melting glass batch materials in a furnace; delivering the molten glass onto a bath of molten tin; pulling the molten glass across the tin bath whereupon the glass is sized and controllably cooled to form a dimensionally stable glass float ribbon; removing the float ribbon from the tin bath; moving the float ribbon by conveying roller through a Lehr to anneal the float ribbon; moving the

float ribbon to a cutting station on conveying rollers where the ribbon is cut into glass sheets, the improvement comprising:

depositing as the float ribbon is formed a photocatalytically-activatable self cleaning coating over said float ribbon which has a major surface and an opposing other major surface, wherein the major surface which contacted the tin bath has tin diffused therein so that the deposition is on the major surface having the diffused tin which forms a sodium ion barrier layer for the photocatalytically-activatable self cleaning coating.

63. A method for producing a layer of titanium dioxide in at least the crystalline phase, wherein said layer of titanium dioxide is a photocatalytically-activatable self-cleaning coating over the glass float ribbon, and further wherein said coating is capable of having a photocatalytically-activated self-cleaning reaction rate of at least about  $2 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$  upon exposure to ultraviolet radiation, said method comprising the steps of:

positioning a chemical vapor deposition coating apparatus over a tin bath containing a glass ribbon having a temperature of at least about  $400^{\circ} \text{ C}$  ( $752^{\circ} \text{ F}$ );

directing a titanium dioxide precursor through said chemical vapor deposition apparatus over a surface of the glass ribbon heated to said temperature; and

thereafter annealing the glass ribbon,

whereby said layer of titanium dioxide is produced.

64. A method according to claim 63, wherein the glass ribbon is at a temperature of at least about  $538^{\circ} \text{ C}$ .

65. A method according to claim 63, wherein the glass ribbon is at a temperature of at least about  $600^{\circ} \text{ C}$ .

66. A method according to claim 63, further comprising the step of exposing the photocatalytically-activatable self-

cleaning coating to ultraviolet radiation whereby a photocatalytically-activated self-cleaning coating is produced.

67. A method according to claim 63, wherein the crystalline phase is at least anatase.

68. A method for producing a glass sheet comprising a layer of titanium dioxide in at least the crystalline phase, wherein said layer of titanium dioxide is a photocatalytically-activatable self-cleaning coating, and further wherein said coating is capable of having a photocatalytically-activated self-cleaning reaction rate of at least about  $2 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$  upon exposure to ultraviolet radiation, said method comprising the steps of:

positioning a chemical vapor deposition coating apparatus over a tin bath containing a glass ribbon having a temperature of at least about  $400^{\circ} \text{ C}$  ( $752^{\circ} \text{ F}$ );

directing a titanium dioxide precursor in a carrier gas stream through said chemical vapor deposition apparatus over a surface of the glass ribbon heated to said temperature; and

thereafter annealing the glass ribbon; and

producing a glass sheet from said annealed glass ribbon, whereby said glass sheet contains said layer of titanium dioxide.

69. A method according to claim 68, wherein the glass ribbon is at a temperature of at least about  $538^{\circ} \text{ C}$ .

70. A method according to claim 68, wherein the glass ribbon is at a temperature of at least about  $600^{\circ} \text{ C}$ .

71. A method according to claim 68, further comprising the step of exposing the photocatalytically-activatable self-cleaning coating to ultraviolet radiation whereby a photocatalytically-activated self-cleaning coating is produced.

72. A method according to claim 68 wherein the directing of the titanium dioxide precursor is directly onto the surface of the glass ribbon without any intervening coating layer.

73. A method according to claim 68 wherein the at least crystalline phase of the titanium dioxide is selected from at least one of anatase, rutile, and brookite crystalline forms of titanium dioxide and wherein an amorphous phase of titanium dioxide may also be present.

74. In a method for forming a glass float ribbon wherein the method includes the steps of melting glass batch materials in a furnace; delivering the molten glass onto a bath of molten tin; pulling the molten glass across the tin bath whereupon the glass is sized and controllably cooled to form a dimensionally stable glass float ribbon; removing the float ribbon from the tin bath; moving the float ribbon by conveying roller through a Lehr to anneal the float ribbon; moving the float ribbon to a cutting station on conveying rollers where the ribbon is cut into glass sheets, the improvement comprising:

depositing over a surface of said float ribbon as the float ribbon is formed in said tin bath by chemical vapor deposition at least a crystalline phase of a photocatalytically-activatable self-cleaning coating,

whereby said glass sheets comprise said photocatalytically-activatable self cleaning coating.

75. A method according to claim 74, further comprising the step of exposing said photocatalytically-activatable self-cleaning coating to ultraviolet radiation in order to provide a photocatalytically-activated self-cleaning reaction rate of at least about  $2 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$ .

76. A method according to claim 74, wherein said crystalline phase comprises titanium dioxide.

77. A method according to claim 74, the improvement further comprising: depositing over a surface of said float ribbon as the float ribbon is formed in said tin bath a sodium ion diffusion barrier layer having a thickness of at least about 100 Å over a surface of said float ribbon and depositing in said tin bath said photocatalytically-activatable self-cleaning coating over said sodium ion diffusion barrier layer.

78. A method according to claim 74 wherein said photocatalytically-activatable self cleaning coating has a thickness in the range of about 100 to 2500 Angstroms.

79. A method according to claim 78, wherein said photocatalytically-activatable self cleaning coating has a thickness in the range of from about 100 to about 1000 Angstroms.

80. A method according to claim 79, wherein said photocatalytically-activatable self cleaning coating has a thickness in the range of from about 100 to about 500 Angstroms.

81. A method according to claim 80, wherein said photocatalytically-activatable self cleaning coating has a thickness in the range of from about 100 to about 400 Angstroms.

82. A method according to claim 81, wherein said photocatalytically-activatable self cleaning coating has a thickness in the range of from about 100 to about 200 Angstroms.

83. A method according to claim 74, the improvement further comprising: depositing a sodium ion diffusion barrier



layer over a surface of said float ribbon as the float ribbon is formed in said tin bath, and depositing said photocatalytically-activatable self-cleaning coating over said sodium ion diffusion barrier layer in said tin bath wherein the sodium ion diffusion barrier layer comprises at least one of amorphous and crystalline phase metal oxides selected from cobalt oxides, chromium oxides, iron oxides, tin oxides, titanium oxides, zirconium oxides, fluorine-doped tin oxides, aluminum oxides, magnesium oxides, zinc oxides, and super-oxides and sub-oxides of any of the foregoing.

84. A method according to claim 83, wherein the sodium ion diffusion barrier layer comprises at least one metal oxide selected from magnesium oxides, aluminum oxides, zinc oxides, tin oxides, and super-oxides and sub-oxides of any of the foregoing.

85. A method according to claim 74, the improvement further comprising: depositing over a surface of said float ribbon as the float ribbon is formed in said tin bath a sodium ion diffusion barrier layer comprising silicone oxide and having a thickness of at least about 100 Å over a surface of said float ribbon and depositing in said tin bath said photocatalytically-activatable self-cleaning coating over said sodium ion diffusion barrier layer.

86. A method comprising the steps of:  
providing by a float manufacturing process a glass article having at least one surface;  
depositing in a tin bath during said float manufacturing process a photocatalytically-activatable self-cleaning coating over the surface of the article by chemical vapor deposition so that the coating has titanium dioxide in at least the crystalline phase and has a thickness ranging from at least 100 Å to less than 1 micron.

87. A method according to claim 86 wherein said photocatalytic reaction rate is determinable as the rate of removal of a stearic acid test film in the range of 100 to 200 Angstroms thick deposited over said photocatalytically-activatable self-cleaning coating wherein said photocatalytic reaction rate is quantitatively determinable as the slope of a curve formed by a plotting of a plurality of Fourier Transform Infrared Spectrophotometer measurements of the integrated intensity of carbon-hydrogen stretching vibrational absorption bands of the stearic acid test film versus an accumulated time of exposure of said photocatalytically-activatable self-cleaning coating to ultraviolet radiation of a frequency within the range of about 300 to 400 nanometers provided by an ultraviolet radiation source positioned over said photocatalytically-activatable self-cleaning coating and having an intensity of about 20 watts per square meter as measured at the surface of the photocatalytically-activatable self-cleaning coating.

88. A method according to claim 86, further comprising the step of exposing the photocatalytically-activatable self-cleaning coating to ultraviolet radiation whereby a photocatalytically-activated self-cleaning coating having a photocatalytically-activated self-cleaning reaction rate of at least about  $2 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$  is produced.

89. A method according to claim 86 wherein said process is selected from a chemical vapor deposition process wherein the article has a minimum temperature to provide sufficient decomposition of the titanium precursor.

112. A process for the production of a titanium dioxide coating having a thickness ranging from about 100 to about 1000 Angstroms on a float glass ribbon, comprising:

manufacturing a continuous float glass ribbon having a first major surface and an opposite major surface defined as a second major surface;

positioning a chemical vapor deposition coating apparatus over the surface of the float ribbon at a point in a tin bath where the float ribbon has a temperature of at least about 400° C;

directing a titanium metal oxide precursor through said chemical vapor deposition apparatus over a surface of the float ribbon in said tin bath, and

annealing the float ribbon

whereby a titanium dioxide coating comprising at least anatase and amorphous phases of titanium dioxide is produced, and wherein

the titanium dioxide coating is a photocatalytically-activatable self-cleaning coating.

113. A process for the production of a titanium dioxide coating according to claim 112, wherein the photocatalytically-activatable self-cleaning coating is capable of having a photocatalytically-activated reaction rate of at least about  $2 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$ .

114. A process for the production of a titanium dioxide coating according to claim 112, wherein the float ribbon has a temperature ranging from about 538° to less than about 800° C.

115. A process for the production of a titanium dioxide coating according to claim 112, wherein said coating is physically durable.

116. A process for the production of a titanium dioxide coating according to claim 112, wherein said coating is resistant to chemical attack.

117. A process for the production of a titanium dioxide coating according to claim 112, wherein the photocatalytically-activatable self-cleaning coating is capable of having a photocatalytically-activated self-cleaning reaction rate of at least about  $5 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$ .

118. A process for the production of a titanium dioxide coating according to claim 112, wherein the photocatalytically-activatable self-cleaning coating is capable of having a photocatalytically-activated self-cleaning reaction rate of at least about  $7.79 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$ .

119. A process for the production of a titanium dioxide coating according to claim 112, wherein the photocatalytically-activatable self-cleaning coating is capable of having photocatalytically-activated self-cleaning reaction rate of at least about  $12.29 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$ .

121. A method comprising the steps of:

providing by a float glass manufacturing process a glass article having at least one surface;

depositing a sodium ion diffusion barrier coating over the surface of the article by chemical vapor deposition in a tin bath during the glass manufacturing process; and

depositing at a temperature in the range of from about  $538^{\circ}$  to below about  $800^{\circ} \text{ C}$  ( $1000^{\circ}$  to  $1472^{\circ} \text{ F}$ ) a photocatalytically-activatable self-cleaning coating over the barrier coating so that the photocatalytically-activatable self-cleaning coating comprises titanium dioxide in at least the crystalline phase and has a thickness ranging from at least about  $100 \text{ \AA}$  to less than 1 micron.

122. A method according to claim 121, wherein the photocatalytically-activatable self-cleaning coating is deposited at a temperature ranging from  $554^{\circ}$  to less than about  $800^{\circ} \text{ C}$  ( $1029^{\circ}$  to  $1472^{\circ} \text{ F}$ ).

### REMARKS

The specification has been amended for 9 items. The specification at page 47 below Table 6 has been corrected for a typographical error changing a reference from 'Sample K' to that of 'Sample J'. Support for this is shown in Table 6 where Sample J has the 400 Angstrom PASC coating and not Sample K. The support for the sentence added at page 7, line 1, is found in the provisional patent application to which the captioned application claims benefit and incorporates by reference. The beginning of this sentence is found at page 14, lines 25-27. The remainder of the sentence is found at page 15, lines 4-6, of the provisional application. Copies of these pages of the provisional application are enclosed.

For items 5 through 8 of the changes to the specification, These added paragraphs were inadvertently not included in Applicants' file copy of the specification. Therefore these paragraphs may not be present in the copy of the application in the USPTO file. If these paragraphs of pages 13 and 15 are present in the USPTO copy, please do not insert these paragraphs again. If the paragraphs of pages 13 and 15 are absent and need to be added, support for pages 13 and 15 are found in the parent patent application. This support in the parent application is at: page 14 line 17 to page 15 line 2; and for the paragraphs of page 15 in the parent application at page 16 line 25 through page 17 line 28.

For the ninth item of the changes to the specification this insertion is from U.S. Patent 4,379,040 column 7 line 42 through column 8 line 44 which was incorporated by reference in the specification at page 12 line 5. A copy of this patent is enclosed herewith.

Support for new claims may be found in the originally-filed disclosure. For example, support for new claims 57-62 may be found in U.S. Patent No. 6,027,766, which is the parent of the present application. Support for a photocatalytically-activatable coating may be found at, *inter alia*, page 17, lines 16-31 of the specification. Support for claims 63-89 may be found at, *inter alia*, page 5 through page

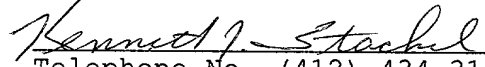
10 of the present specification. Support for claims 112-119 and 121-122 may be found in, *inter alia*, the claims as originally filed in this application and Example 1. Support for claim 115 may be found at, *inter alia*, page 5, line 24 of the specification. Support for claim 116 may be found at, *inter alia*, page 5, line 25 of the specification. Photocatalytic reaction rates set forth in claims 117-119 find support in, *inter alia*, first paragraph of page 6, and Table 6. Exemplary support is also provided in the table at pages 23-24 of the Amendment filed August 24, 2001. No new matter has been added.

Applicants respectfully submit the present claims are patentable over the art of record. An early and favorable action on the merits is earnestly solicited.

Attached hereto is a marked-up version of the amendments to the specification and the claims made by the instant amendment. The attached page is captioned **"VERSION WITH MARKINGS TO SHOW CHANGES MADE"**.

Respectfully submitted,

KENNETH J. STACHEL, ESQ.  
Registration No. 27,722  
Attorney for Applicant

  
Telephone No. (412) 434-3186  
Facsimile No. (412) 434-4292

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**VERSION WITH MARKINGS TO SHOW CHANGES MADE**

**IN THE DISCLOSURE**

Paragraph beginning on page 1 at line 5 has been amended to read as follows:

This application is a divisional of U.S. Application Serial No. 09/282,943 filed April 1, 1999, which is a divisional of U.S. Non-provisional Application Serial No. 08/899,257 filed July 23, 1997, now U.S. Patent No. 6,027,766, which claims the benefit of U.S. Provisional Application Serial No. 60/040,566 filed March 14, 1997. U.S. Provisional Application Serial No. 60/040,565 filed March 14, 1997, and U.S. Regular Application No. \_\_\_\_\_08/899,265 to Greenberg et al., entitled "Photocatalytically-Activated Self-Cleaning Appliances", filed even date herewith, now U.S. Patent No. 6,054,227 are also related to the present application and are hereby incorporated by reference.

1) Paragraph beginning at page 5, line 33, has been amended as follows:

The PASC coating 24 must be sufficiently thick so as to provide an acceptable level of PASC activity. There is no absolute value which renders the PASC coating 24 "acceptable" or "unacceptable" because whether a PASC coating has an acceptable level of PASC activity is largely determined by the purpose and conditions under which the PASC coated article is being used and the performance standards selected in connection with that purpose. In general, thicker PASC coatings provide higher PASC activity. However, other considerations may weigh toward a thinner coating, e.g. thinner coatings are preferred when the article is to have high transmission for aesthetic or optical reasons; the surface contaminants on the surface of the article are easily removed with a thinner PASC coating, the coating is exposed to substantial irradiation and/or the PASC coating 24 will be exposed to sodium ion

poisoning discussed in more detail below. In a CVD process, a photocatalytically-active self-cleaning coating 24 is formed which may range from about 100Å to 2500Å thick. For a wide variety of applications, it is preferred that the PASC coating is at least about 200 Angstroms (Å), preferably at least about 400Å and more preferably at least about 500Å thick. It has been found that when the substrate 22 is a piece of float glass and the PASC coating 24 is an anatase titanium dioxide PASC coating formed directly over the piece of float glass by the CVD method, that a thickness of at least about 500Å provides a PASC reaction rate in the range of about  $2 \times 10^{-3}$  to about  $5 \times 10^{-3}$  per centimeter minute (hereinafter " $\text{cm}^{-1}\text{min}^{-1}$ ") for the removal of a stearic acid test film when the PASC coating was exposed to ultraviolet radiation from a light source such as that sold under the tradename UVA-340 by the Q-Panel Company of Cleveland, Ohio, having an intensity of about 20 watts per square meter (hereinafter  $\text{W/m}^2$ ) at the PASC coating surface which is acceptable for a wide range of applications.

2) Paragraph beginning at page 47, line 6, has been amended as follows:

The results of the photocatalytic analysis shown in Table 6 suggest that a titanium dioxide layer thickness of about 625Å with no barrier layer (Sample I) can approach the PASC activity of a thinner 400Å PASC coating over an SIDB layer (Sample KJ). It should be noted that for Samples KJ, the SIDB layer underwent an intermediate cooling and subsequent reheating operation described, which reheating operation may have reduced the SIDB layer effectiveness for Sample KJ, which might otherwise have had a higher PASC activity.

3) The paragraph beginning at page 15, line 5, has been amended as follows:

Referring now to Fig. 2, in an alternative method of preventing sodium ion poisoning of the PASC coating, an SIDB layer



26 is provided between the PASC coating 24 and the substrate 22. The SIDB layer 26 may be the only layer between the PASC coating 24 and the substrate 22, or it may be one layer of a multilayer stack. Where a multilayer stack is employed, it is not required that the SIDB layer 26 be in contact with the substrate 22, provided the SIDB layer 26 is positioned between the PASC coating 24 and the substrate 22 to prevent sodium ion numeral 27 as depicted in Fig. 2 migration from the substrate 22 to the PASC coating 24.

4) The paragraph beginning at page 28, line 1, has been amended as follows:

The decreased PASC activity of Example 2 is believed to arise from the difference in titanium dioxide coating thickness between Examples 1 and 2, (about 2100Å versus about 700-800Å, respectively). More particularly, it is believed that the PASC reaction rate of Example 2 was lower than that of Example 1 due to the increased depth of sodium ion diffusion into the titanium dioxide coating of Example 2 as a larger percentage of the total thickness of the titanium dioxide PASC coating for the titanium dioxide PASC coating of Example 2 than that of Example 1. It is believed that sodium ions migrated from the glass sample into the PASC coating of Example 2 in annealing ~~lehr 44~~ zone 98. One conclusion that may be drawn from a comparison of Examples 1 and 2 is that in the absence of an SIDB layer, thicker PASC coatings are less susceptible to sodium ion poisoning, thus maintaining higher PASC activity.

5) Also if not already present in the captioned patent application, please replace the paragraph beginning at page 12, line 29 with the following paragraph and include the additional paragraphs following this rewritten paragraph as follows:

The preferred method to provide a PASC coating using the MSVD method is to sputter a coating on the substrate, remove the coated substrate from the MSVD coater and thereafter heat treat the

coated substrate to crystallize the sputter coating into the PASC coating 24. For example, but not limiting to the invention, with the MSVD method, a target of titanium metal sputtered in an argon/oxygen atmosphere having about 5-50%, preferably about 20% oxygen, at a pressure

\*of about 5-10 millitorr to sputter deposit a titanium dioxide coating of desired thickness on the substrate 22. The coating as deposited is not crystallized. The coated substrate is removed from the coater and heated to a temperature in the range of about 400°C (752°F) to about 600°C (1112°F) for a time period sufficient to promote formation of the PASC crystalline form of titanium dioxide to render PASC activity. Generally at least an hour at temperature in the range of about 400°C (752°F) to about 600°C (1112°F) is preferred. Where the substrate 22 is a glass sheet cut from a glass float ribbon, the PASC coating 24 may be sputter deposited on the air side and/or the tin side.

The substrate 22 having the PASC coating 24 deposited by the CVD, spray pyrolysis or MSVD methods may be subsequently subjected to one or more post-PASC coating annealing operations to increase the self-cleaning activity of the PASC coating 24. It is believed that such post-PASC coating annealing may increase self-cleaning activity of the PASC coating 24 by promoting formation of the desired PASC crystalline phase. As may be appreciated, the time and temperatures of the anneal may be affected by several factors, including the makeup of substrate 22, the makeup of PASC coating 24, the thickness of the PASC coating 24, and whether the PASC coating 24 is directly on the substrate 22 or is one layer of a multilayer stack on substrate 22. It has been determined that where the substrate 22 is a piece of float glass and the PASC coating is a 400Å or 625Å thick anatase titanium dioxide formed by the spray pyrolysis method, that annealing the coating at 500°C (932°F) for up to 13 minutes increased PASC activity.

6) The section of the paragraph beginning at page 14 line 1 and ending on page 14 line 3 has been amended as follows:

As discussed above, whether the PASC coating is provided by the CVD process, the spray pyrolysis process or the MSVD process, where the substrate 22 includes sodium ions that can migrate from substrate 22 into the PASC coating deposited on substrate 22, the sodium ions may inhibit or destroy the photocatalytic activity of the PASC coating by forming inactive compounds while consuming titanium e.g. by forming sodium titanates or by causing recombination of photoexcited charges.--

7) The paragraph beginning on page 14 line 10 has been amended with the following rewritten paragraph which includes additional sentences and which is followed by an additional paragraph:

It has been found that when the thickness of the PASC coating exceeds a minimum threshold value, the PASC activity is not destroyed by sodium ion migration even though the PASC coating is deposited over the surface of a sodium-ion containing substrate while the substrate is at a temperature sufficient to cause migration of sodium ions from substrate into the PASC coating. While the mechanism for this result is not completely understood, it is believed that when the thickness of the PASC coating exceeds this minimum thickness, the sodium ions are able to migrate only through a fraction of the overall thickness of the PASC coating during the time period at which the temperature of substrate exceeds the temperature which permits sodium ion migration. Thereafter, when the temperature of substrate falls below that which causes sodium ion migration, the sodium ions migration stops or "freezes" in place, resulting in a thickness of the PASC coating opposite from the substrate surface free of sodium ion poisoning and able to maintain PASC activity. This minimum thickness of the PASC coating as may be appreciated by those skilled in the art varies with expected parameters such as, but not limited to, the time at which substrate is held above the temperature at which sodium ion migration occurs, the use to which the PASC article of manufacture is to be put and the degree of PASC activity desired or required.

It has been found that for a CVD deposited titanium dioxide PASC coating over a piece of soda-lime-silica flat glass, the thickness of the PASC coating should be a minimum of about 250Å, preferably a minimum of about 400Å and more preferably a minimum of about 500Å to permit a sufficient portion of the PASC coating 24 to remain free of sodium ion poisoning and retain its PASC activity.

Referring now to Fig. 2, in an alternative method of preventing sodium ion poisoning of the PASC coating, an SIDB layer 26 is provided between the PASC coating 24 and the substrate 22. The SIDB layer 26 may be the only layer between the PASC coating 24 and the substrate 22, or it may be one layer of a multilayer stack. Where a multilayer stack is employed, it is not required that the SIDB layer 26 be in contact with the substrate 22, provided the SIDB layer 26 is positioned between the PASC coating 24 and the substrate 22 to prevent sodium ion migration from the substrate 22 to the PASC coating 24.

8) The section of the paragraph that begins on page 16 line 1 and ends on page 16 line 9 has been amended as follows:

The SIDB layer 26 may be formed of amorphous or crystalline metal oxides including but not limited to cobalt oxides, chromium oxides and iron oxides, tin oxides, silicon oxides, titanium oxides, zirconium oxides, fluorine-doped tin oxides, aluminum oxides, magnesium oxides, zinc oxides, and mixtures thereof. Mixtures include but are not limited to magnesium/aluminum oxides and zinc/tin oxides. As can be appreciated by those skilled in the art, the metal oxide may include oxides, super-oxides or sub-oxides of the metal. While the thickness of the SIDB layer necessary to prevent sodium ion poisoning of the PASC coating varies with several factors including the time period at which a substrate will be maintained at temperatures above which sodium ion migration occurs, the rate of sodium ion migration from the substrate, the rate of sodium ion migration through the SIDB layer, the thickness of the PASC coating and the degree of photocatalytic activity required for a given application, typically for most applications,

the SIDB layer thickness should be in the range of at least about 100Å, preferably at least about 250Å and more preferably at least about 500Å thick to prevent sodium ion poisoning of the PASC coating layer. The SIDB layer may be deposited over substrate 22 by CVD, spray pyrolysis, or MSVD methods. Where the spray pyrolysis or CVD methods are employed, the substrate 22 is preferably maintained at a temperature of at least about 400°C (752°F) to ensure decomposition of the metal-containing precursor to form the SIDB layer. The SIDB layer may be formed by other methods, including the sol-gel method, which sol-gel method as noted above is not compatible with the manufacture of a glass float ribbon.

9) At page 12 of the captioned patent application at line 28 after the word "method", please insert the following paragraphs from U.S. Patent 4,379,040 column 7 line 42 through column 8 line 44 which was incorporated by reference in the specification at page 12 line 5:

-- It was customary to attain a desired degree of oxidation in titanium oxide films by an evaporation technique carried out in two distinct stages; first, by depositing titanium oxide in an under-oxidized state and thereafter, by introducing an oxidizing atmosphere thereto to attain the desired degree of oxidation. It has been found according to the present invention that the titanium oxide can be successfully magnetically enhanced sputtered onto the substrate with the degree of oxidation desired, thus eliminating the need for further oxidation. Deposition of ideally oxidized titanium oxide films is also more easily controlled in the practice of the present invention than heretofore, yielding a more consistent final product. It is believed that the preferred titanium oxide films deposited according to the present invention comprise a combination of titanium dioxide intermixed with atoms and/or small agglomerations of titanium metal, i.e. films of titanium oxide having greater than 1.7 but less than 2.0 parts oxygen to parts titanium, and preferably between 1.9 and 2.0. Such films may be characterized as having an optical extinction

coefficient between about 0.03 and 0.3, preferably between 0.03 and 0.09, and most preferably between 0.06 and 0.08. The titanium oxide layer is preferably deposited with a thickness within the range of about 200 to 500 Angstroms to obtain the desired optical properties and film continuity.

The titanium oxide layer can be deposited according to the present invention by magnetically sputtering a titanium metal cathode in an evacuated atmosphere having partial pressures of oxygen and argon. Initially, the coating chamber 12 is evacuated to less than  $3 \times 10^{-5}$  torr, after which an atmosphere of about 75% argon and 25% oxygen at a total pressure of about  $6 \times 10^{-4}$  torr is established. The cathode is activated at a preselected constant electrical power, and the deposition rate and total chamber pressure are established at preselected values. Upon reaching the desired coating conditions, the cathode is scanned across the surface of the substrate at a preselected rate to deposit a thin layer of an ideally oxidized film thereon. The luminous transmittance of the substrate is monitored during deposition by the photometer and photoelectric cell and decreases as the thickness of the film increases, from an initial value of about 90% for a glass substrate. Deposition rate, and therefore the degree of oxidation of the deposited titanium oxide film, is maintained constant either cyclically, or continuously, utilizing the embodiment of the invention. Deposition of the titanium oxide layer can be terminated when the luminous transmittance decreases to a value between about 72% and 76%, (about 80% to 85% of the transmittance of the uncoated substrate) a condition which is usually reached with a film thickness between about 300 Å and 350 Å, entailing about 5 to 7 passes of the cathode over the substrate. Generally during the above-described procedure, the oxygen input rate is gradually increased to compensate for decreasing amounts of outgassing from the coating chamber. The titanium oxide layer can have an optical extinction coefficient between about 0.06 and 0.08 upon deposit, according to the present invention. --

**IN THE CLAIMS**

Claim 1 has been canceled without prejudice.

Claims 57-89, 112-119, 121 and 122 have been added as follows:

57. A method comprising the steps of:

manufacturing a continuous glass float ribbon having a first major surface and an opposite major surface defined as a second major surface, the first major surface having tin diffused therein characteristic of forming the glass float ribbon on a molten tin bath,

positioning a chemical vapor deposition coating apparatus over the surface of the float ribbon at a point in the manufacture of the float ribbon where the float ribbon has a temperature of at least about 400° C (752° F);

directing a metal oxide precursor selected from the group consisting of titanium tetrachloride, titanium tetraisopropoxide and titanium tetraethoxide in a carrier gas stream through said chemical vapor deposition apparatus over a surface of the float ribbon and annealing the float ribbon to produce titanium dioxide in the crystalline phase as a photocatalytically-activatable self-cleaning coating over the glass float ribbon,

whereby said coating is capable of having a photocatalytically-activated self-cleaning reaction rate of least about  $2 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$ .

58. A method comprising the steps of:

manufacturing a continuous glass float ribbon having a first major surface and an opposite major surface defined as a second major surface, the first major surface having tin diffused therein characteristic of forming the glass float ribbon on a molten tin bath;

depositing a photocatalytically-activatable self-cleaning coating over at least one of the major surfaces by positioning a spray pyrolysis coating apparatus over the surface of the float ribbon at a point in the manufacture of the float ribbon where the

float ribbon has a temperature of at least about 400° C (752° F), directing an aqueous suspension of titanyl acetylacetonate and wetting agent in an aqueous medium, wherein the concentration of the titanyl acetylacetonate is in the range from about 5 to about 40 weight percent of the aqueous suspension, through said spray pyrolysis coating apparatus over a surface of the float ribbon and annealing the float ribbon in air to produce titanium dioxide in the crystalline phase as a photocatalytically-activatable self-cleaning coating over the glass float ribbon, whereby said coating is capable of having a photocatalytically-activated self-cleaning reaction rate of at least about  $2 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$ .

59. In a method for forming a glass float ribbon wherein the method includes the steps of melting glass batch materials in a furnace; delivering the molten glass onto a bath of molten tin; pulling the molten glass across the tin bath whereupon the glass is sized and controllably cooled to form a dimensionally stable glass float ribbon; removing the float ribbon from the tin bath; moving the float ribbon by conveying roller through alehr to anneal the float ribbon; moving the float ribbon to a cutting station on conveying rollers where the ribbon is cut into glass sheets, the improvement comprising:

depositing by a process selected from the group consisting of spray pyrolysis and chemical vapor deposition a crystalline phase of a photocatalytically-activatable self-cleaning coating over a surface of said float ribbon as the float ribbon is formed, whereby said coating is capable of having a photocatalytically-activated self-cleaning reaction rate of at least about  $2 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$ .

60. A method comprising the steps of:

providing a glass article having at least one surface by a float manufacturing process;

depositing a photocatalytically-activatable self-cleaning coating over the surface of the article by a process selected from the group consisting of chemical vapor deposition and spray pyrolysis during the glass manufacturing process so that the coating



has titanium dioxide in the crystalline phase and has a thickness in the range of at least 200 Å and less than 1 micron whereby said coating is capable of having a photocatalytically-activated self-cleaning reaction rate of at least about  $2 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$ .

61. A method comprising the steps of:

providing an article of manufacture having at least one surface;

depositing a sodium ion diffusion barrier layer by a process selected from the group consisting of chemical vapor deposition, magnetron sputtered vacuum deposition (MSVD), and spray pyrolysis having a thickness of at least 100 Å over said surface; and

depositing a photocatalytically-activatable self-cleaning coating by a process selected from the group consisting of chemical vapor deposition, MSVD, and spray pyrolysis over said sodium ion diffusion barrier layer whereupon said sodium ion diffusion barrier layer inhibits migration of sodium ions from the surface of said article to said photocatalytically-activatable self cleaning coating.

62. In a method for forming a glass float ribbon wherein the method includes the steps of melting glass batch materials in a furnace; delivering the molten glass onto a bath of molten tin; pulling the molten glass across the tin bath whereupon the glass is sized and controllably cooled to form a dimensionally stable glass float ribbon; removing the float ribbon from the tin bath; moving the float ribbon by conveying roller through a Lehr to anneal the float ribbon; moving the float ribbon to a cutting station on conveying rollers where the ribbon is cut into glass sheets, the improvement comprising:

depositing as the float ribbon is formed a photocatalytically-activatable self cleaning coating over said float ribbon which has a major surface and an opposing other major surface, wherein the major surface which contacted the tin bath has tin diffused therein so that the deposition is on the major surface having the diffused tin

which forms a sodium ion barrier layer for the photocatalytically-activatable self cleaning coating.

63. A method for producing a layer of titanium dioxide in at least the crystalline phase, wherein said layer of titanium dioxide is a photocatalytically-activatable self-cleaning coating over the glass float ribbon, and further wherein said coating is capable of having a photocatalytically-activated self-cleaning reaction rate of at least about  $2 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$  upon exposure to ultraviolet radiation, said method comprising the steps of:

positioning a chemical vapor deposition coating apparatus over a tin bath containing a glass ribbon having a temperature of at least about  $400^{\circ} \text{ C}$  ( $752^{\circ} \text{ F}$ );

directing a titanium dioxide precursor through said chemical vapor deposition apparatus over a surface of the glass ribbon heated to said temperature; and

thereafter annealing the glass ribbon,  
whereby said layer of titanium dioxide is produced.

64. A method according to claim 63, wherein the glass ribbon is at a temperature of at least about  $538^{\circ} \text{ C}$ .

65. A method according to claim 63, wherein the glass ribbon is at a temperature of at least about  $600^{\circ} \text{ C}$ .

66. A method according to claim 63, further comprising the step of exposing the photocatalytically-activatable self-cleaning coating to ultraviolet radiation whereby a photocatalytically-activated self-cleaning coating is produced.

67. A method according to claim 63, wherein the crystalline phase is at least anatase.

68. A method for producing a glass sheet comprising a layer of titanium dioxide in at least the crystalline phase, wherein said layer of titanium dioxide is a photocatalytically-activatable self-

cleaning coating, and further wherein said coating is capable of having a photocatalytically-activated self-cleaning reaction rate of at least about  $2 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$  upon exposure to ultraviolet radiation, said method comprising the steps of:

positioning a chemical vapor deposition coating apparatus over a tin bath containing a glass ribbon having a temperature of at least about  $400^{\circ} \text{ C}$  ( $752^{\circ} \text{ F}$ );

directing a titanium dioxide precursor in a carrier gas stream through said chemical vapor deposition apparatus over a surface of the glass ribbon heated to said temperature; and

thereafter annealing the glass ribbon; and

producing a glass sheet from said annealed glass ribbon,

whereby said glass sheet contains said layer of titanium dioxide.

69. A method according to claim 68, wherein the glass ribbon is at a temperature of at least about  $538^{\circ} \text{ C}$ .

70. A method according to claim 68, wherein the glass ribbon is at a temperature of at least about  $600^{\circ} \text{ C}$ .

71. A method according to claim 68, further comprising the step of exposing the photocatalytically-activatable self-cleaning coating to ultraviolet radiation whereby a photocatalytically-activated self-cleaning coating is produced.

72. A method according to claim 68 wherein the directing of the titanium dioxide precursor is directly onto the surface of the glass ribbon without any intervening coating layer.

73. A method according to claim 68 wherein the at least crystalline phase of the titanium dioxide is selected from at least one of anatase, rutile, and brookite crystalline forms of titanium dioxide and wherein an amorphous phase of titanium dioxide may also be present.

74. In a method for forming a glass float ribbon wherein the method includes the steps of melting glass batch materials in a furnace; delivering the molten glass onto a bath of molten tin; pulling the molten glass across the tin bath whereupon the glass is sized and controllably cooled to form a dimensionally stable glass float ribbon; removing the float ribbon from the tin bath; moving the float ribbon by conveying roller through a lehr to anneal the float ribbon; moving the float ribbon to a cutting station on conveying rollers where the ribbon is cut into glass sheets, the improvement comprising:

depositing over a surface of said float ribbon as the float ribbon is formed in said tin bath by chemical vapor deposition at least a crystalline phase of a photocatalytically-activatable self-cleaning coating,

whereby said glass sheets comprise said photocatalytically-activatable self cleaning coating.

75. A method according to claim 74, further comprising the step of exposing said photocatalytically-activatable self-cleaning coating to ultraviolet radiation in order to provide a photocatalytically-activated self-cleaning reaction rate of at least about  $2 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$ .

76. A method according to claim 74, wherein said crystalline phase comprises titanium dioxide.

77. A method according to claim 74, the improvement further comprising: depositing over a surface of said float ribbon as the float ribbon is formed in said tin bath a sodium ion diffusion barrier layer having a thickness of at least about 100 Å over a surface of said float ribbon and depositing in said tin bath said photocatalytically-activatable self-cleaning coating over said sodium ion diffusion barrier layer.

78. A method according to claim 74 wherein said photocatalytically-activatable self cleaning coating has a thickness in the range of about 100 to 2500 Angstroms.

79. A method according to claim 78, wherein said photocatalytically-activatable self cleaning coating has a thickness in the range of from about 100 to about 1000 Angstroms.

80. A method according to claim 79, wherein said photocatalytically-activatable self cleaning coating has a thickness in the range of from about 100 to about 500 Angstroms.

81. A method according to claim 80, wherein said photocatalytically-activatable self cleaning coating has a thickness in the range of from about 100 to about 400 Angstroms.

82. A method according to claim 81, wherein said photocatalytically-activatable self cleaning coating has a thickness in the range of from about 100 to about 200 Angstroms.

83. A method according to claim 74, the improvement further comprising: depositing a sodium ion diffusion barrier layer over a surface of said float ribbon as the float ribbon is formed in said tin bath, and depositing said photocatalytically-activatable self-cleaning coating over said sodium ion diffusion barrier layer in said tin bath wherein the sodium ion diffusion barrier layer comprises at least one of amorphous and crystalline phase metal oxides selected from cobalt oxides, chromium oxides, iron oxides, tin oxides, titanium oxides, zirconium oxides, fluorine-doped tin oxides, aluminum oxides, magnesium oxides, zinc oxides, and super-oxides and sub-oxides of any of the foregoing.

84. A method according to claim 83, wherein the sodium ion diffusion barrier layer comprises at least one metal oxide selected from magnesium oxides, aluminum oxides, zinc oxides, tin oxides, and super-oxides and sub-oxides of any of the foregoing.

85. A method according to claim 74, the improvement further comprising: depositing over a surface of said float ribbon as the float ribbon is formed in said tin bath a sodium ion diffusion barrier layer comprising silicone oxide and having a thickness of at least about 100 Å over a surface of said float ribbon and depositing in said tin bath said photocatalytically-activatable self-cleaning coating over said sodium ion diffusion barrier layer.

86. A method comprising the steps of:  
providing by a float manufacturing process a glass article having at least one surface;  
depositing in a tin bath during said float manufacturing process a photocatalytically-activatable self-cleaning coating over the surface of the article by chemical vapor deposition so that the coating has titanium dioxide in at least the crystalline phase and has a thickness ranging from at least 100 Å to less than 1 micron.

87. A method according to claim 86 wherein said photocatalytic reaction rate is determinable as the rate of removal of a stearic acid test film in the range of 100 to 200 Angstroms thick deposited over said photocatalytically-activatable self-cleaning coating wherein said photocatalytic reaction rate is quantitatively determinable as the slope of a curve formed by a plotting of a plurality of Fourier Transform Infrared Spectrophotometer measurements of the integrated intensity of carbon-hydrogen stretching vibrational absorption bands of the stearic acid test film versus an accumulated time of exposure of said photocatalytically-activatable self-cleaning coating to ultraviolet radiation of a frequency within the range of about 300 to 400 nanometers provided by an ultraviolet radiation source positioned over said photocatalytically-activatable self-cleaning coating and having an intensity of about 20 watts per square meter as measured at the surface of the photocatalytically-activatable self-cleaning coating.

88. A method according to claim 86, further comprising the step of exposing the photocatalytically-activatable self-cleaning coating to ultraviolet radiation whereby a photocatalytically-activated self-cleaning coating having a photocatalytically-activated self-cleaning reaction rate of at least about  $2 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$  is produced.

89. A method according to claim 86 wherein said process is selected from a chemical vapor deposition process wherein the article has a minimum temperature to provide sufficient decomposition of the titanium precursor.

112. A process for the production of a titanium dioxide coating having a thickness ranging from about 100 to about 1000 Angstroms on a float glass ribbon, comprising:

manufacturing a continuous float glass ribbon having a first major surface and an opposite major surface defined as a second major surface;

positioning a chemical vapor deposition coating apparatus over the surface of the float ribbon at a point in a tin bath where the float ribbon has a temperature of at least about  $400^{\circ} \text{ C}$ ;

directing a titanium metal oxide precursor through said chemical vapor deposition apparatus over a surface of the float ribbon in said tin bath, and

annealing the float ribbon

whereby a titanium dioxide coating comprising at least anatase and amorphous phases of titanium dioxide is produced, and wherein

the titanium dioxide coating is a photocatalytically-activatable self-cleaning coating.

113. A process for the production of a titanium dioxide coating according to claim 112, wherein the photocatalytically-activatable self-cleaning coating is capable of having a photocatalytically-activated reaction rate of at least about  $2 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$ .

114. A process for the production of a titanium dioxide coating according to claim 112, wherein the float ribbon has a temperature ranging from about 538° to less than about 800° C.

115. A process for the production of a titanium dioxide coating according to claim 112, wherein said coating is physically durable.

116. A process for the production of a titanium dioxide coating according to claim 112, wherein said coating is resistant to chemical attack.

117. A process for the production of a titanium dioxide coating according to claim 112, wherein the photocatalytically-activatable self-cleaning coating is capable of having a photocatalytically-activated self-cleaning reaction rate of at least about  $5 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$ .

118. A process for the production of a titanium dioxide coating according to claim 112, wherein the photocatalytically-activatable self-cleaning coating is capable of having a photocatalytically-activated self-cleaning reaction rate of at least about  $7.79 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$ .

119. A process for the production of a titanium dioxide coating according to claim 112, wherein the photocatalytically-activatable self-cleaning coating is capable of having photocatalytically-activated self-cleaning reaction rate of at least about  $12.29 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$ .

121. A method comprising the steps of:  
providing by a float glass manufacturing process a glass article having at least one surface;  
depositing a sodium ion diffusion barrier coating over the surface of the article by chemical vapor deposition in a tin bath during the glass manufacturing process; and



depositing at a temperature in the range of from about 538° to below about 800° C (1000° to 1472° F) a photocatalytically-activatable self-cleaning coating over the barrier coating so that the photocatalytically-activatable self-cleaning coating comprises titanium dioxide in at least the crystalline phase and has a thickness ranging from at least about 100 Å to less than 1 micron.

122. A method according to claim 121, wherein the photocatalytically-activatable self-cleaning coating is deposited at a temperature ranging from 554° to less than about 800° C (1029° to 1472° F).